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SOLVENT EFFECTS IN ORGANIC CHEMISTRY

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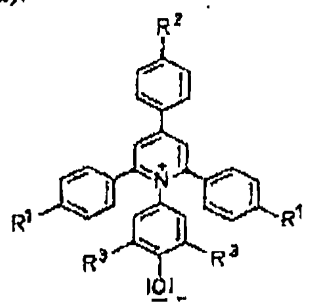
characteristic of the solvent and R gives the susceptibility of the given property towards a change of solvent. As a standard process, Brownstein [65] chose the CT absorption of Kosower's dye [55], and assigned to it an R-value of 1.00. Having chosen a standard solvent and a standard reaction, it was then possible to calculate R and S-values for other reactions and solvents, respectively. From Kosower's work, 58 S-values were used to determine R-values for 9 reactions. In a continuation of this process, 158 S-values and 78 R-values were deduced, including R-values for solvent-dependent UV/Vis, IR, and NMR absorptions, rates of reactions, and positions of equilibria [65]. The S-values represent statistical averages of a variety of different solvent polarity parameters, including Z and Y, and therefore, cannot be related to a specific model process. In principle, this is an interesting attempt at generalization but many of the correlations used to calculate R and S-values are rather poor. It would seem that too many different solvent-dependent processes are being mixed-up and treated in an oversimplified way.

The practical limitations in the Z-value approach can be overcome by using pyridinium-N-phenoxide betaine dyes such as *(29a)* as the standard. They exhibit a strongly solvatochromic $\pi-\pi^*$ absorption band with intramolecular charge-transfer character (*cf.* discussion of this dye in Section 6.2.1, its UV/Vis spectrum in Fig. 6-2, and its dipole moment in electronic ground and excited state mentioned in Table 6-1, dye no. 12).



(29a): $R^1 = R^2 = H$; $R^3 = C_6H_5$
(29b): $R^1 = R^2 = CH_3$; $R^3 = C_6H_5$
(29c): $R^1 = R^2 = CH_3$; $R^3 = C(CH_3)_3$
(29d): $R^1 = H$; $R^2 = Br$; $R^3 = C_6H_5$

Dimroth and coworkers [66] have proposed a solvent polarity parameter, $E_T(30)$, based on the transition energy for the longest-wavelength solvatochromic absorption band of the pyridinium-N-phenoxide betaine dye *(29a)* (dye no. 30 in reference [66]). According to Eq. (7-22), the $E_T(30)$-value for a solvent is simply defined as the transition energy of the dissolved betaine dye *(29a)* measured in kcal/mol [2, 66–68] (for conversion into SI units see footnote on page 237). The major advantage of this approach is that the solvatochromic absorption band is at longer wavelengths for *(29a)* than for Kosower's dye, generating an extraordinarily large range for the solvatochromic behavior (from $\lambda = 810$ nm, $E_T(30) = 35.3$, for diphenylether, to $\lambda = 453$ nm, $E_T(30) = 63.1$, for water). Since the greater part of this solvatochromic range lies within the visible region of the spectrum, it is even possible to make a visual estimation of solvent polarity. For example, the solution color of *(29a)* is red in methanol, violet in ethanol, green in acetone, blue in isoamyl alcohol, and greenish-yellow in anisole [66]. A remarkable feature of these solution color changes is that nearly every color of the visible spectrum can be obtained by applying suitable binary mixtures of solvents of different polarity. To date, the betaine dye *(29a)* holds the world record in solvatochro-

mism with a hypsochromic shift of more than 350 nm (ΔE_T *ca.* 28 kcal/mol = 117 kJ/mol) in the case of a solvent change from diphenylether to water. Owing to this exceptionally large displacement of the solvatochromic absorption band, the $E_T(30)$-values provide an excellent and very sensitive characterization of the polarity of solvents, high $E_T(30)$-values corresponding to high solvent polarity. $E_T(30)$-values have been determined for more than 100 pure solvents [2, 66], and for a number of binary solvent mixtures [68–72, 72a]. A collection of $E_T(30)$-values representing the most comprehensive empirical solvent polarity scale so far known is given in Table 7-3.

Table 7-3. Empirical parameter of solvent polarity, $E_T(30)$, based on the solvatochromism of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide (betaine dye no. 30 in reference [66]), measured at 25 °C and 760 torr.

Solvents	$E_T(30)$ [kcal/mol]
Water	63.1
2,2,2-Trifluoroethanol	59.5
2,2,3,3-Tetrafluoro-1-propanol	59.4
Glycerol	57.0[a)]
Formamide	56.6
1,2-Ethanediol	56.3
Methanol	55.5
1,3-Propanediol	54.9[b)]
1,2-Propanediol	54.1[a)]
N-Methylformamide	54.1
Diethylene glycol	53.8
Ethanol/Water (80:20)	53.7
Triethylene glycol	53.5
2-Methoxyethanol	52.3
N-Methylacetamide	52.0[c)]
Ethanol	51.9
2-Aminoethanol	51.8
Acetic acid	51.2[d)]
Benzyl alcohol	50.8
1-Propanol	50.7
1-Butanol	50.2
2-Methyl-1-propanol, Isobutyl alcohol	49.0
2-Propanol	48.6
Cyclopentanol	47.7
2,6-Dimethylphenol	47.6
2-Butanol	47.1
3-Methyl-1-butanol, Isoamyl alcohol	47.0
Cyclohexanol	46.9
4-Methyl-1,3-dioxol-2-one, Propylene carbonate	46.6
2-Pentanol	46.5
Nitromethane	46.3
Acetonitrile	46.0
3-Pentanol	45.7
Dimethylsulfoxide	45.0
Aniline	44.3
Tetra-*n*-hexylammonium benzoate	44.3
Tetrahydrothiophene-1,1-dioxide	44.0
2-Methyl-2-propanol, *tert*-Butyl alcohol	43.9[c)]